Dissolution of the Rock During Smart Water Injection in Heavy Oil Carbonate Reservoirs by Natural Generation of Acidic Water

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ABSTRACT: Smart waters have been studied for enhanced oil recovery in carbonate reservoirs, gaining significant attention from research groups and oil industry companies. However, there is general consensus that the complexity of the fluids/rock system is governing the effects, much fundamental knowledge is lacking and many questions and uncertainties remain. For instance, existence of rock dissolution in carbonate rocks, as a mechanism for oil production, has previously been documented. This work specially focused on the interaction oil-brine-rock and its effect on rock dissolution. Carbonate rocks (limestones and dolomites), brines and heavy crude oils were individually analyzed and then systematically mixed with each other to gain a comprehensive understanding of their interactions. Five heavy crude oils with different properties were tested under similar reservoir conditions (≈ 92° C). Results revealed the generation of acidic water derived from the interaction between injected fluids and crude oils. Not all crude oils could produce the acidic water, which is the cause of rock dissolution. This research suggests that the chemical interaction between crude oil and injected water may be one of the main reasons for the increased efficiency in response to the use of the smart waters for the improvement of oil production. Basic analyses that are presented here essentially provide an insight into the impact of the chemical interaction between crude oil and injection water with the rock. Finally, coreflood experiments were performed using a dolomitic core in order to monitor and verify the presence of dissolution during the flow of fluids. A basic crude oil was selected for this purpose. Effluent analysis, pH measurements and permeability evaluations corroborated the influence caused by smart waters injection as acidic water in contact with the rock. The findings of these experiments prove that is possible to predict and control the occurrence of the dissolution observing interactions of crude oil and injection water.

INTRODUCTION

The use of (smart) water injection as a natural wettability modifier has recently gained significant attention. By definition, smart water has been adopted as the idea of changing the injected brine composition in order to enhance oil recovery (EOR) in oil reservoirs. To date, seawater has been incorporated as a part of this group of smart waters, due to its important role of being a natural wettability modifier. Complex analysis such as micromodel tests, coreflood and spontaneous imbibition experiments and zeta potential, interfacial tension or contact-angle measurements have been extensively run to explain the success of smart water for enhanced oil recovery methods.[1-3] Most of the studies on smart water injection have been conducted with light oils and have been focused on both sandstone and carbonate reservoirs. The results of the range of investigations which have been carried out, some of them contradictory, have allowed us to hypothesise certain mechanisms which are believed to be responsible for the good oil recovery factors. There are numerous technical papers on this topic, in which researchers have proposed many mechanisms, but it is not clear from the various references which mechanism or mechanisms work in specific rocks, fluids or conditions.[4-6]

Computational programs, robust or unsophisticated, have also been used to simulate and represent such experimental results. Those same tools have subsequently been used to predict, find or validate previous mechanisms stated. However, sometimes, the answers to complex enquiries cannot be dealt with by advanced tools or sophisticated experiments. First, we must learn to walk before we can run.

One important consideration in the selection of a water composition for enhanced oil recovery in carbonate reservoirs is the compatibility between the elements of each system and the injected fluids. Interaction of the injected water with the rock and native fluids may affect the natural state of the system.[7-8] The details of the interactions between reservoir fluids and injected fluids or injected fluids and rock can vary widely depending on the composition of such elements. For this reason, the interactions between

these elements should be meticulously evaluated before and after each experiment. Simple and practical analyses could reveal the level of complexity and at the same time improve understanding of the mechanism/s believed to underlie the good recovery factors obtained with smart water. The complete evaluation of the fluid/rock interactions would thus lead to a better picture of such mechanisms.

The goal of this research will concentrate on studying the simplest interactions between the formation and injected fluids and the rock. In a series of experiments, carbonate rocks (fragments of cores), brines and crude oils were individually analysed and then systematically mixed with each other in order to gain a comprehensive understanding of their interactions at two temperatures, with a special focus on the rock dissolution. Representing three fluids and predicting their interactions with each other and subsequently with the rocks presents a problem that is not easy to solve. In this work, practical analyses helped to elucidate the real importance of the crude oil/injection water interactions.

EXPERIMENTAL SECTION

Characterisation of Crude Oils. Different heavy oil samples were selected from a group of reservoirs and tested in this work. Table 1 shows the basic properties of the crude oils. The total acid and base numbers are also presented. The crude oils were centrifuged before being used, to ensure they were free from solid particles or emulsions. Wax or other deposits were not observed in the crude oil samples. The composition of the original crude oils was also determined in terms of asphaltenes, resins, aromatics and saturates. Although some analyses of metals and sulphur content of certain crude oils were obtained, they will be presented later. The crude oil samples were also studied using a gas chromatography-flame ionisation method for determination of carbon number distribution (CND).

Table 1. Crude Oil Properties.

Crude Oil	Density* (^{o}API)	Viscosity* (cp)	Asphaltene Content (% wt)	Water Content (ppm)*	Resins Content (% wt)	TAN (mgKOH/g)*	TBN (mgKOH/g)*
A	14.12	53,484.31	13.20	208.40	31.70	1.00	3.50
B	12.49	71,253.86	27.78	302.46	28.29	0.17	4.23
C	15.44	295,328.67	24.00	2,619.30	17.6	0.35	4.60
D	32.18	15.60	-	199.00	-	0.21	0.21
E	19.27	1,251.80	0.82	2,920.52	16.85	2.40	2.10

*Measured at 20^{o} C.

Preparation of Brines. Brines were reformulated from the original compositions in the laboratory, using distilled water and salts. Four brine solutions (FW, SW, LSSW10 and LSSW50) with different compositions were prepared for this work. In order to have a reference system for some experiments, distilled water (DW) was also used. The seawater used for the experiments was from the Gulf of Mexico. Table 2 depicts the composition of each brine. Seawater (SW) brine contains significant amounts of Ca^{2+}, Mg^{2+} and SO_4^{2-} ions but the formation brine (FW) brine only contains small amounts of Mg^{2+} and SO_4^{2-}.

Core. The work has been performed on a dolomite rock. The dimensions were as follows: diameter of 5.09 cm, length of 15.20 cm, a pore volume of 58.15 cc and a porosity and permeability of 18.80 % and 142.21 mD, respectively. The Environmental Scanning Electron Microscope (ESEM) exhibited the presence of carbon, oxygen, magnesium and calcium with small amounts of iron and silicon. Although the presence of sulphate was not detected using the ESEM, chemical analysis of the effluents during the water saturation validated the existence of sulphate into the rock.

Cleaning of rock fragments. Toluene and methanol were used for the removal of water and the elimination and cleaning of organic material in the cores.

Ionic Composition Analysis. A compact ion chromatograph (883 Basic IC plus) manufactured by Metrohm, was employed to obtain the ionic concentrations of the effluents after the water injection experiments. Prior to the analysis, all the water samples were centrifuged and diluted to 1:100 using distilled water and the ion concentrations were calculated based on standard solutions.

Viscometer. A temperature-controlled viscometer (VISCOlab 3000) was used for viscosity measurements at different temperatures. The device is equipped with an integrated heater that allows precision for the viscosity readings at specific temperatures (from slightly above ambient to 180^{o} C). It provided an accuracy of ± 1.0 % and was suitable for the crude oils in this research.

Density meter. A DM 40 density meter from Mettler Toledo was employed to measure the density of the oil/water samples accurately. The instrument was able to calculate the density at temperatures between 15 and 100^{o} C.

Titration. The C20 Karl Fisher titration method was applied for measuring the water content in the crude oil samples at room conditions. In all tests the measurements were corroborated to verify their accuracy and repeatability.

pH Measurements. Due to the variations of pH of the water samples during the experiments, a pH measurement instrument, S400 produced by Mettler Toledo, was utilised to measure the pH deviations. All the water samples were free of organic compounds from the crude oils.

Interaction of Formation Water and Injection Water. The formation brine was mixed with each of the others with ratios from 10/90 to 90/10, respectively. The new solutions were left at either 20° C or 92° C for one week for equilibration and to visually observe any changes or formation of salts. This protocol was repeated at least twice for each new solution generated.

Interaction of Crude Oil and Injection Water. A very similar procedure to that described by Gachuz-Muro et al.[7] was used for this case, in which the crude oils were brought in contact with some working brines at two temperatures, 20 and 92° C. Brines were prepared with different compositions. They were then brought into contact with crude oils and the samples were aged for one week at the two temperatures. The samples were periodically shaken and then both samples were left for equilibration at room temperature. Finally, the samples were centrifuged. Measurements of the basic properties for both fluids were at room conditions (20° C).

Rock/Injection Water Interaction. One preliminary way to elucidate if mineral dissolution is really participating in the rock/fluid interactions it is to use a geochemical modelling program capable of simulating or predicting a wide range of chemical reactions between rock and water.

In this subsection, PHREEQC program was used to evaluate the chemical mineral dissolution and precipitation between the rock and the injected water.

Crude Oil/Brines/Rock Interactions. The problem of representing a system which involves 3 fluids; crude oil, formation water and fluid of injection, or predicting their interactions with each other and with the rock, is that sometimes particular assumptions are or should be taken into account. The approach to this difficulty can be simplified by showing how they can act under static conditions, assuming a coreflood experiment, and events at specific times. Figure 1 displays this sequence: (a) at the start of the injection, when formation fluids and rock are still in equilibrium; (b) when the injection of water begins (in fact, this period cannot be represented for these experiments, because the system has not changed); (c) later, when the core contains equal volumes of formation water, crude oil and injected water, and finally (d) when it is assumed that the formation water has been completely displaced from the core and that there are only residual oil and water of injection.

The tests evaluate pH alteration and ionic concentration changes for given crude oil/ brine/rock combinations, Figure 2. To establish these relationships between such elements, a number of practical experiments were devised to meet this need. Tests were conducted at static conditions and high temperature (92° C). First, 250 ml glass bottles containing 100 ml of formation water, a mix of formation water/injected water and injected water (LSSW10), respectively, were left for one week at high temperature (1). After this period, these brines were cooled down and their pH

Table 2. Brine Compositions.

Ion	FW (mg/L)	SW (mg/L)	LSSW10 (mg/L)	LSSW50 (mg/L)
Na^+	9,614.97	11,429.38	1,142.93	228.58
Ca^{2+}	320.36	429.60	42.96	8.59
Mg^{2+}	218.94	1361.60	136.16	27.23
K^+	-	351.10	35.11	7.02
Ba^{2+}	-	0.01	-	-
Sr^{2+}	-	8.37	0.83	0.16
Cl^-	15,117.25	20,040.00	2,004.00	400.80
SO_4^{2-}	550.63	3,500.00	350.00	70.00
HCO_3^-	1,135.9	47.58	4.75	0.95
TDS (mg/l)	25,670.86	37,198.14	3,719.81	743.96
pH (adim)*	8.01	7.80	7.20	6.75
Viscosity (cp)*	1.03	1.07	1.00	0.99

*Measured at 20° C.

measured. A previously cleaned fragment of rock was then added to each glass bottle and equilibrated for one week more (2). Next, the glass bottles were withdrawn from the oven, and a water sample was taken for IC analysis and pH values were measured again. Then, a crude oil was added to the bottles and equilibration was allowed (3). Once the glass bottles were removed from the oven, a sample of water was taken with special needle syringes and filtered; the fluids were later collected and centrifuged to fully separate the crude oils and brines. Finally, measurements of pH and ion concentration were taken. The measurements of the values were performed at room temperature. The procedure was repeated twice and verified by comparisons between static and dynamic conditions. Dynamic conditions were produced by applying mechanical agitation to the bottles containing the samples for some minutes.

Interaction of Formation Water and Injection Water. There was no precipitation under different volume fractions either at 20° C or at 92° C. It was concluded that the low salinity waters and seawater would not cause any precipitation in contact with the formation brine.

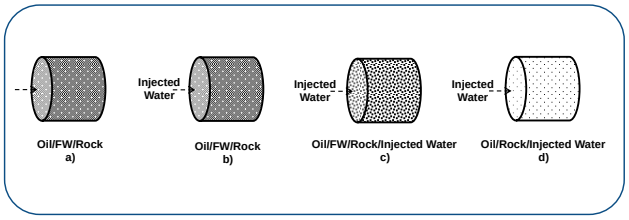

Figure 1. Sequence representing a coreflood experiment at static conditions, a) System in equilibrium, b) System before the injection (in equilibrium), c) System with equal volumes of fluids, d) System with residual oil and fluid of injection.

Interaction of Crude Oil and Injection Water. The crude oil showed changes in viscosity, density and water content. For instance, water content increased for each sample after the contact and the metal content of each crude oil sample also clearly showed variations in concentration, as shown in Table 3. Whilst LSSW10 gained much more calcium, magnesium and sodium, the use of seawater with the crude oil "A" got to some extent the mentioned metals. This would initially indicate that the water tends to be suspended in the crude oil. The water could have been then retained by two mechanisms: a) chemically by asphaltenes and resins and b) by viscous retention of water droplets.[9]

Coreflood Experiments. As a part of the project of this research, a novel high pressure and high temperature setup was designed in-house to facilitate coreflood experiments (up to 150 °C and 10,000 psi). The temperature-controlled oven houses all the lines, cells with injection fluids, transducers, the core holder and additional instruments. The orientation of core for the different experiments was horizontal and it was maintained at approximately the same overburden pressure (OB) during the whole evaluation. Transducers and pumps were verified internally and calibrated, if it was necessary, before the start of each coreflood experiment. A pair of pumps was used for controlling the brine cells and another pair of pumps for controlling the pressure in the oil cells, while one more pair of pumps was used for the overburden pressure and back pressure regulator (BPR). Note that, for these experiments, the brine cells contain specific working fluids, and the oil cell contains extra-heavy crude oil.

In all of experiments, when the oil production stopped, a change in the injection rate was applied to make sure that there was no more mobile oil. The oil volume (expressed as a percentage of the original oil in place) was measured as a function of pore volume injected. The experiments confirmed additional oil recovery when smart fluids were injected in secondary mode. Some tests had an additional coreflood experiment in order to evaluate the repeatability of the results. They were consistent with the first estimations.

When the coreflood experiment was finished, the core was then cleaned with appropriate solvents (toluene or methanol) for removing organic material and residual water at high temperature.

RESULTS AND DISCUSSION

Examination of the analyses of crude oils indicated a relatively high variation in their internal structures, as shown in Figure 3. This method allows crude oil samples to be quantitatively compared with a relatively similar matrix for specific compounds. Results of % weight *vs.* carbon number distribution for each crude oil sample were plotted from C_{30} to C_{70} (where the heavy compounds are mainly found). The CND data for ≥ C_{30} showed a variation of their % weights. In particular, from C_{45} to C_{70}, low salinity water turned out to be more important, indicating that there was a significant change in the crude oil after the contact: there was an increase in the values of the weight. In contrast, the values for crude oil samples in contact with seawater, remained slightly lower from C_{38} to C_{59}, while from C_{61} to C_{70} their values coincided with those for the original crude oils.

This clearly indicates structural changes due to brine/crude oil interactions for the heaviest compounds.

Structural changes of the crude oils may occur when they are in contact with low salinity fluids.[8] Although the results shown in Table 3 and the trends observed in Figure 3 are in line with the Alvarado´s findings[8], these observations are not studied in this study because it is assumed that those effects (microdispersions) are more important for the flow of fluids and transport.

The analyses of the water also indicated variations of its pH, showing more acidic conditions for brines in contact with crude oils. Figure 4 shows the values obtained for five types of water which were left at 92° C. Black cylinders represent the original values before contact with the crude oils. The pH values of the formation water did not undergo any change; they were in equilibrium with the crude oils.

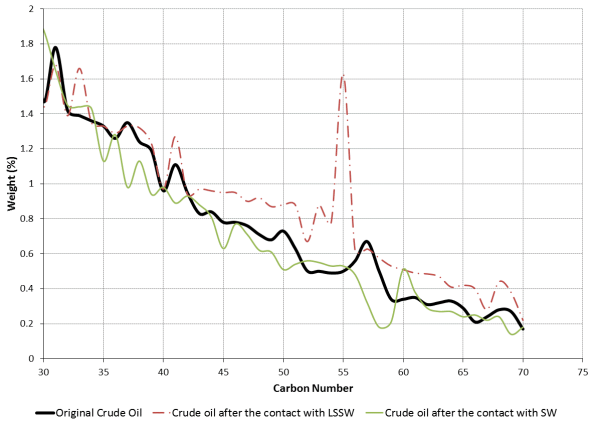

Figure 3. Variation of the crude oil structures after contact with water.

When salts are removed from the brines, in this case from seawater, there will be natural reactions involving the original brine and compounds found in crude oils, resulting in the formation of new and different type of waters. Note that the used crude oils have high total base numbers, except crude oil "E" which is more acidic.

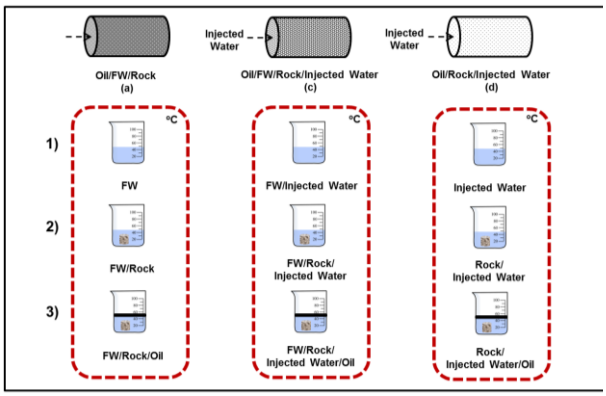

Figure 2. Procedure for evaluating changes in the composition of the fluids and pH values. Interactions among fluids and rock under static.

Considering these preliminary results, a new set of experiments was developed under static condition where fluids, crude oils and working brines were all in contact at the same temperatures.

Let us take two crude oils, one acidic and one more basic. The results are rather similar, as can be seen in Figure 5. When crude oils and diluted brines (LSSW10) were shaken together, the pH values did not vary significantly (from 3.59 to 3.70 at 20 and 92° C, respectively). When the fluids were not shaken, once again, the pH values did not change (from 3.92 to 3.98 at 20 and 92° C, respectively).

Although this simple evaluation revealed a pattern in the results, it is presumed that temperature could have not had a large effect on the interactions between crude oil and brine, even when the fluids were in static conditions. This would mean that there is a natural interaction between injected waters and crude oil leading to a transfer of certain compounds, independently of the movement of the fluids.

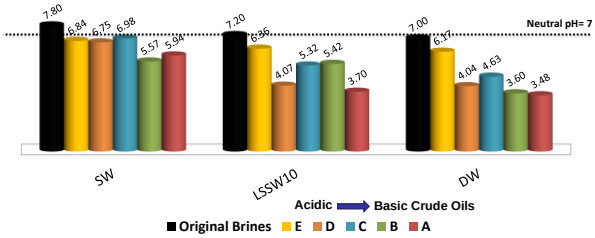

Figure 4. pH values for brines samples after the contact with crude oils.

This was not very noticeable when high salinity water (seawater) was in contact with specific crude oils in the earlier experiments. However, although migration occurs, it is not as important as when salts are eliminated from brines. Basic crude oils are playing an important role at this point.

Table 3. Water and Metal Content Present in the Crude Oil Samples, Crude Oil "A".

Crude Oil Samples	Water Content (ppm)*	Metal Content (mg/kg)*			
		Ca^{2+}	K^{+}	Mg^{2+}	Na^{+}
Crude Oil "A"	208.40	5.40	0.80	0.80	9.80
Crude Oil "A" in contact with SW	2,023.36	6.70	0.90	3.30	26.80
Crude Oil "A" in contacted with LSSW10	6,216.23	10.00	3.20	11.80	94.30

*Measured at 20° C.

Nasralla et al.[1-3] revealed similar variations of the pH behaviour in their experimental work, but they were not able to associate such findings with the purpose of their work, which was to study the effect of the pH on the electrical charges. In 2014, they conducted experiments with a high total base number and presented the results for six brines in contact with this crude oil. Three pH values dropped a little, seawater brine kept its value almost constant and the pH of two brines was lowered from their original values.

Reactions Influencing the pH Variation of the Injected Water. To understand how new types of water could be formed, it is necessary to know how the crude oil interacts with water. Water is a highly structured liquid with ions and an extensive network of hydrogen bonds.[10] The type of ions is an important aspect, as they can either decrease or increase the solubility of organic materials in the water.

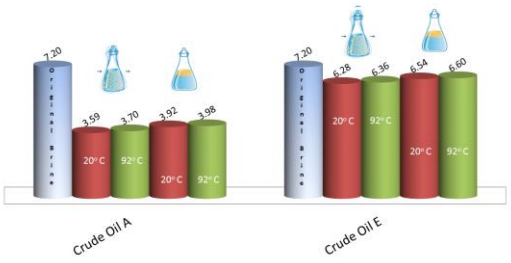

Figure 5. pH values for brine samples after contact with crude oils at different conditions and temperatures.

Collins and Washabaugh[11] described the terms "structure makers and breakers" in a biophysical context. Nevertheless, the use of these concepts has been accepted and utilised in a diversity of scientific fields where water is studied. Marcus[10] organised the ions according to their effects on the water structure. In this work, the ions related to the common effects on formation water, injected water and crude oils by metal and non-metal compounds will be considered:

•Breaking ions (chaotropes): I^-, Br^-, K^+, Rb^+, Cs^+, Cl^-, N^{3-}, S^{2-}, Se^{2-}, Ra^{2+}

•Borderline Ions: Na^+, Ag^+, Ba^{2+}, Pb^{2+}, F^-, HCO_3^-

•Making ions (kosmotropes): Li^+, Cu^+, Au^+, Sr^{2+}, Al^{3+}, Cr^{3+}, OH^-, Ca^{2+}, CO^{3+}, Pu^{4+}, V^{2+}, Cr^{2+}, Mn^{2+}, Cu^{2+}, Cd^{2+}, V^{3+}, Fe^{3+}, Mg^{2+}, CO^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}

When a significant amount of salts is dispersed in a liquid, they will considerably affect the solubility of a gas or another liquid in that solvent. If this solubility is less than that in salt-free water, this occurrence is called the "salting-out effect".[12] If the solubility increases with the reduction of salt concentrations, then the phenomenon is called the "salting-in effect". This description is very basic because it overlooks the role of the ions. However, ions, either kosmotropes or chaotropes, like to undertake important reactions with water, thereby leaving fewer free water molecules. The kosmotropic solutes are ions with small radius and high surface charge density. Calcium and magnesium are good examples of strong kosmotropes. The chaotropic solutes are longer ions with smaller surface charge density. For instance, this would indicate that calcium and magnesium will reduce the solubility of other solutes and chloride or sodium would help to extend the solubility of these solutes, such as water-soluble fractions from crude oils.

On the other hand, the crude oils are very complex mixtures of hydrocarbons and can be different from one reservoir to another, and many of these are inadequately characterised, due to their attributes. Crude oils may be classified based on their chemical structures or physical properties. The latter are much easier to measure than are chemical structures.[13] Hughey et al.[14] identified around 11,000 individual compounds in one crude oil, but their individual detection is hard, which is why the identification of hydrocarbon groups is more commonly employed.

The hydrocarbons in crude oils which contain only hydrogen and carbon can be divided into two main groups: a) aliphatic (alkanes, alkenes, alkynes and cyclialiphatics) and b) aromatics. It should be recalled that hydrocarbons such as alkanes, alkenes and aromatics are "water insoluble" because they have non-polar fractions. There are many other organic compounds, which contain nitrogen, oxygen and sulphur.[13]

Crude oils also contain appreciable amounts of such organic non-hydrocarbon compounds with sulphur, nitrogen and oxygen (these combine with long ring structures to form resins and asphaltenes) and in smaller quantities, metal components in solution and inorganic salts in colloidal suspension. Even though the concentrations of compounds such as carbon dioxide or hydrogen sulphide in certain fractions may be quite small, their influence is important in other crude oils, especially in heavy crude oils.

A simpler criterion can be to arbitrarily group crude oils with similar characteristics, for example, into four general fractions: saturates, aromatics, resins and asphaltenes (SARA technique). Resins and asphaltenes are considered as the most active compounds in crude oils because they contain polar components. These components have fractions with basic and acidic functionalities. Nitrogen compounds are the main fractions of basic components in crude oils and generally fall within the range of 0.1 to 0.9 %, although they may represent up to 3 %.

The asphaltenes group contains large molecules and which are less water-soluble. Resins have smaller molecules and contain acids and bases that are more water-soluble. Acidic crude oil components, sometimes termed as naphthenic acids (RCOOH), exhibit activity and are part of resin fractions. The naphthenic acids' total content in crude oils is commonly determined by potentiometric titration and expressed as Total Acid Number (TAN). The smallest molecular weight acids are dissolved in the aqueous phase, whilst the larger naphthenic acid molecules are oil-soluble. However, some of them may be water-soluble at high pH.[15-14] Naphthenic acid frequently describes all carboxylic acids present in crude oils and when they have three rings they are said to be more hydrophilic (water-loving) than acids with one or two rings.[18] Water-solubility is related to pKa (pH>pKa, negatively charged molecule) and pKb (pH<pKb, positively charged molecule is created), relating to the acid and base respectively. The strength of an acid (pKa) denotes the tendency of a molecule to give up or remove a proton to water at a specific pH. Most carboxylic acids have a pKa, between 3 and 5. Moreover, all carboxylic acids, whether insoluble or soluble in water, react

in the presence of NaOH or KOH and other strong bases to form salts. Naphthenic acids also contribute to the formation of emulsions and soaps (in enhanced oil recovery), affecting the surface tension between reservoir fluids and alkaline solutions.[19-22]

A good example of this reaction between water and crude oil is the injection of surfactants to the reservoirs. Alkali injection is a process in which water is injected into the reservoirs at an elevated pH (10 to 12) value to improve oil recovery. The effect of the water prepared with chemical compounds is partially due to the chemical reaction between this added product and organic acids that are found in the crude oils. If the (alkaline) aqueous phase is in contact with the crude oil, there is a reaction which can form surfactants (soaps) and emulsification. Consequently, the capillary pressure between the oil phase and the injected solution may be reduced, producing a lower interfacial tension (IFT), and hence allowing displacement of the residual oil towards the producing wells. McGuire et al.[23] proposed that low salinity water and alkaline injection act in a similar way.

At reservoir conditions, the pH of the formation water is around 5-8, so the majority of the water-soluble acids (85 %) are expected to be dissolved in the water, but their dissolution will also depend on the composition of the reservoir water.[24] In general, if the pH of the solution is 2 units higher than the pKa, then the acid will be nearly 100 % ionized. This fact determines that the carboxylic acids are either diffused in an aqueous solution or better placed in relation to the crude oil/water interface. In this way, each carboxylic acid will be present totally as its anion, at the crude oil/water interface (reaction 1).

$$RCOOH + H_2O \Leftrightarrow RCOO^- + H_3O^+ \quad (1)$$

As the H^+ concentration is higher in such aqueous solutions, the pH will be lower, creating a very acidic environment. Therefore, in the current experiments, the reactions of migration of the acidic components (salting-in effect), when crude oils and water were in contact, were mainly controlled by the composition of the water and its pH. As the pH of the injected brine exceeded the pKa for the acid compounds from the crude oil, the acids and water-soluble compounds, tended to dissociate and change into negatively charged molecules. For this reason, as shown in Figure 4, such acidic compounds became more water-soluble and active in both low salinity (LSSW10) and pure water (DW), except for seawater which turned out to be only important for the crude oils "A" and "B". As a result, the presence of polar compounds creates *acidic waters* which may dissolve the carbonated rock. Crude oils with low TAN were especially prone to create such *acidic waters* (Figure 4). The reason for the higher pH of the crude oil "E" after contact is that it has the lowest amount of water-soluble acidic compounds. Therefore, Crude oil "E" may contain larger acid molecules (oil-soluble components) than the other crude oils. The *acidic water* created by oil/ injected water interaction is practically impossible to detect or observe, even in laboratory experiments, because the effluents (produced water from experiments) give high pH values. This phenomenon is just perceptible when crude oil is in contact with injected waters.

Carbonates have a positive charge for pH values lower than the point of zero charge, which can be considered ~8. The measured pHs are below of their point of zero charges, and consequently, the acidic compounds (oil-soluble acids) in heavy crude oils should be adsorbed in the rock because heavy oils contain higher volumes of both resins and asphaltenes. The natural state of wettability should then be mixed or oil wet, which is in line with several studies that have reported contact angle measurements indicating that carbonate reservoirs are usually more oil wet than reservoirs with silica.[25,26]

Due to all these descriptions, and as reservoir fluids and rock are equilibrium, we can assume that:

1.- Under high salinity water injection (formation water), the salting-in effect is not important, because the crude oil/formation water/rock system keeps its balance and stability, except for specific crude oils where a drop of pH is observed, as shown in Figure 6a. In general, high salinity water tends to remain closely associated with the rock and reservoir fluids, preserving an equilibrium state.

2.- If a low salinity fluid is injected, there will be a transition zone in which this water is mixed with formation brine, generating new water with different characteristics. Although that generated water may contain fewer ions, the crude oil compounds will barely diffuse (Figure 6b). This is especially important because the different concentrations between the formation water and the injected water will contribute less to the oil recovery. In Figures 6a and 6b, it can be seen that the rock/water and crude oil/water interfaces are still in equilibrium and they are negatively charged at high pH. According to some authors,[27-30] the electrical properties may change as a function of the pH and the composition of the injected fluid and the crude oil, suggesting changes at both interfaces.

3.- Subsequently, when the area has been completely invaded by low salinity water, the loss of ions causes a collapse in the system (at this point, according to Le Chatelier's principle, the system has to be re-established) and leads to better dissociation of the acidic compounds, which may migrate or be diffused into the current water or reside at the crude oil/water interface (*salting-in mechanism*), Figure 6c. The low salinity water or pure water associated with more hydrogen ions will then act as *acidic water* (*new water begins forming*). The system therefore has to compensate the crude oil compounds for the loss of hydrogen ions. The hydrogen ions may be replaced by other reactive ions of metals such as magnesium, calcium, potassium or sodium, so the water-soluble compounds again undergo an association process. This is in good agreement with the results in Table 3. Usually, potassium, sodium, calcium and magnesium react with water and acids, and are regarded as more reactive than the hydrogen ion.

Moreover, many studies have postulated that the rock/brine and crude oil/brine interfaces will be positively

charged because of the low pH value.[27-30] Due to the presence of two interfaces with the same positive charges, a natural electrostatic force of repulsion will occur between rock/brine and crude oil/brine interfaces[29] and the rock surface will then release the crude oil drops (*change of wettability*) which tend to mainly be ionised by positive ions, Figure 6c. The crude oil/water interface captures more positive ions such as calcium and magnesium, contributing to the formation of stable and strong regions around the crude oil drops.

4.- As the carbonated formation is being exposed to the aggressive action of this acidic water, the *rock dissolution mechanism* will immediately take place where the crude oil has been released and in areas exposed to direct contact with formation water (Figure 6d). As soon as *rock dissolution* occurs, the pH of this *acidic water* will increase gradually and be adjusted because ions (bicarbonates) are being liberated from the rock. The produced water will probably be a mixture of dissolved hydrocarbons, additional amounts of ions from the rock and existing ion concentrations in the formation and injected water. Additionally, the crude oil drops could suffer internal modifications such as changes of their structure, viscosity and density variations or disparities in their amount of water. These assumptions are also in line with the findings shown in Table 3 and the Figure 6, presented above. Recent studies have given an idea about the structural changes of crude oils brought about by contact with low salinity fluids, thus opening a debate regarding a new mechanism for smart water.[7,8]

5.- Finally, at some point, *the natural generation of acidic water* will decline, due to the absence of crude oil and the pH from the produced water should become higher but more constant.

Based on this reasoning, *generation of acidic water* may be responsible for part of the low salinity water effects observed in carbonate rocks. Thus, it is plausible to believe that more than two mechanisms can simultaneously occur in low salinity water injection for these types of formations. The *generation in-situ* of these types of *acidic waters* will depend on the amount of crude oil present in the cores or maybe even in the reservoirs. It also depends on the presence of hydrogen concentrations that are transferred to the waters. The model in Figure 6 supports the assumption that basic crude oils were susceptible to donating hydrogen ions in the cases analysed.

For the acidic crude oil examined, the migration was minimal, resulting in an absence of acidic water (Figure 4).

Nevertheless, one cannot generalise that the proposed model is applicable to all basic crude oils or unsuitable for all acidic crude oils. The components of oils dictate what kind of interactions will occur in oil reservoirs. In many cases, oil and gas reservoirs contain non-hydrocarbon constituents, such as carbon dioxide, nitrogen or hydrogen sulphide.[13] Some of these can be soluble in the reservoir water and can also influence an adjustment of the pH. For instance, a decrease in salinity of the water improves the solubility of carbon dioxide (CO_2), causing a lower pH[31] under certain pressure and temperature conditions. When CO_2 is dissolved in water, a small proportion of it reacts chemically with this water to make carbonic acid, H_2CO_3. This, likewise, causes the possibility of producing dissolution from the carbonated rock. As can be seen, the synergy between crude oils and injected waters is likely to be greater than other interactions.

Rock/Injection Water Interaction. PHREEQC is designed to perform a wide variety of aqueous geochemical calculations. PHREEQC implements several types of aqueous models, including Davies' equation (an extension of the Debye–Hückel equation) and Pitzer equation. Davies' equation is limited for calculations with low-salinity waters, although works reasonably well in sodium chloride solutions like seawater [32-34]. In this paper, we compare both equations with the intention of estimating its future usefulness.

The saturation index (SI) is defined as:

$$SI = \log(IAP/K), \quad (2)$$

Where IAP is the ion activity product and K is the equilibrium constant. The variation of the equilibrium constant with temperatures is here calculated using the Van't Hoff equation. The saturation index is a useful quantity to determine whether the water is saturated (SI=0), undersaturated (SI<0) or supersaturated (SI>0) with respect to the given mineral. It can be a relatively simple way of quantifying if a particular mineral may thermodynamically dissolve or precipitate under certain conditions.

Limestone is composed mainly by calcite whereas dolostone contains dolomite. The presence of other minerals, such as quartz and clay minerals is scarcer. As a consequence, we consider calcite, for the limestone system; and dolomite, for the dolostone system. The systems considered were closed systems, where only the brine and the given minerals were in contact.

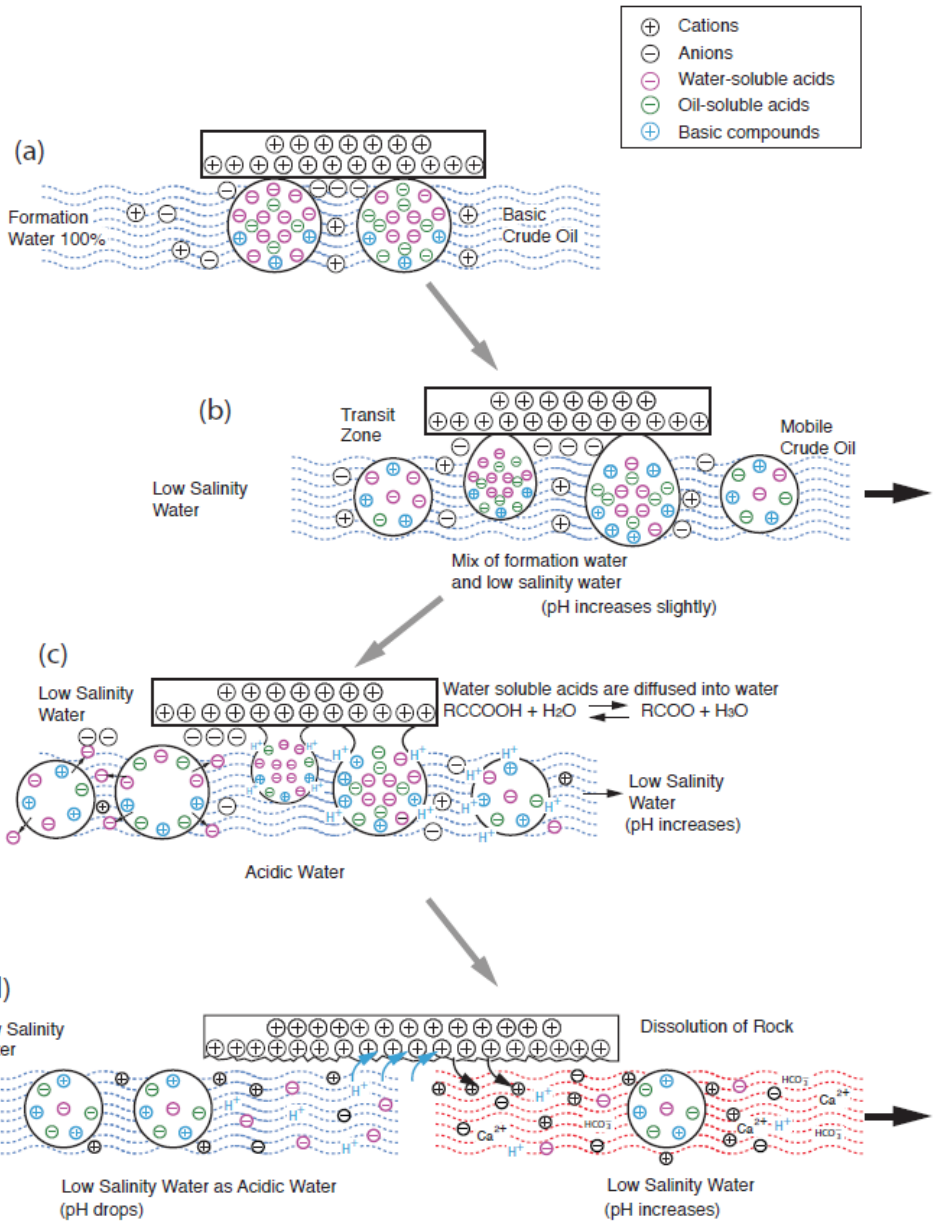

Figure 6. Sequence of effects in a system that is under injection with low salinity water.

The phase equilibrium option was run for six brines, SW (pH= 7.80), LSSW10 (pH= 7.20), LSSW50 (pH=6.75) and seawater, low salinity water which had previously been in contact with two crude oils (SWCCOA, LSSWCCOA and LSSWCCOE with pH~5.94, ~3.70 and ~6.36, respectively). These last ones were artificially generated by bringing a volume of SW and LSSW10 into contact with crude oil "A" and crude oil "E", which were reported to generate acidic water than using unaltered original water. After the contact, the new waters (SWCCOA, LSSW10CCOA and LSSW10CCOE) were separated and filtered.

Table 4 indicates the possible dissolution of these mineral samples for the most of the systems, especially with the LSSWCCOA and LSSW50 brines. Note the saturation index values calculated using Davies' and Pitzer's equations are similar in seawater and the rest of the brines. Dolomite is supersaturated in the seawater, although its precipitation is kinetically hindered. Temperature appears to

play an important role for the seawater cases as saturation indexes for calcite and dolomite increase from 25 to 50 ºC.

Additionally, the theoretical or maximum amount of precipitated or dissolved material, expressed in terms of mass, and the corresponding pH values of the brines were also determined (Table 5). Here, the second and fourth columns are relevant. In the closed systems, the dissolved amounts are expected to be unimportant, excluding the low salinity water contacted by crude oil "A", which is more aggressive. Based on the PHREEQC calculations, the pHs would be all higher, with exception of that of seawater, which is about 0.2 units higher at 25° C. These results imply that dissolution at pH ≤ 6.5 is higher compared to that at pH ≥ 6.5.

Table 4. Saturation Index Calculated for Two Minerals (Solid Species) in Contact with Different Types of Injection Water.

	PHREEQC	PITZER	PHREEQC	PITZER
Tempt.	25° C		50° C	
Brine	Calcite			
SW	-0.17	-0.23	0.07	0.04
SWCCOA	-1.90	-1.96	-1.60	-1.66
LSSW10	-2.25	-2.34	-1.95	-2.04
LSSWCCOA	-5.01	-5.09	-4.68	-4.75
LSSWCCOE	-3.08	-3.17	-2.77	-2.86
LSSW50	-4.10	-4.18	-3.78	-3.86
Brine	Dolomite			
SW	0.55	0.57	1.18	1.28
SWCCOA	-2.90	-2.88	-2.16	-2.12
LSSW10	-3.64	-3.67	-2.89	-2.90
LSSWCCOA	-9.17	-9.17	-8.35	-8.32
LSSWCCOE	-5.31	-5.34	-4.53	-4.55
LSSW50	-7.34	-7.70	-6.55	-6.56

At the same time, the calcium, magnesium and bicarbonate concentrations in the brines were obtained before and after the interaction with the minerals. The graphs in Figure 7 and Figure 8 depict the simulated results for calcite and dolomite. As we can see, the major change in the brines' composition is that they now have higher Ca^{2+}, Mg^{2+} and HCO_3^- values, where the original concentrations were about 42.96, 136.16 and 4.75 ppm (or mg/L), respectively. The main reason for the increase in HCO_3^- is that the program calculates the concentrations of this ion based on the initial pH. The modification in the initial conditions (manipulated pH) changes the concentration of these sensitive species.

These species are now present in the LSSWCCOA in higher concentrations, although they were lower before reaction with calcite and dolomite, as described. In this case, the added amount of bicarbonate in the solution, from 4.7 to 1,150 ppm (calcite), could be increasing the pH of this particular brine (from 3.7 to 6.09), but it is not clear why the variation of their pH values occurs for the other brines, because the dissolved amount is minimal.

Crude Oil/Brines/Rock Interactions. As mentioned and described above, dissolution may occur where there is no movement of fluids. For the PHREEQC calculations, pH and ionic concentrations of the solutions naturally increased during the contact between rocks and fluids and under no-flow conditions. To confirm the effect of the possible dissolution, a second step should involve tests when this effect could be observed under static conditions, as PHREEQC assessed the potential for dissolution using different waters.

Table 5. Dissolved Amount of Minerals (per Kilogram of Water) and pH Variation Using PHREEQC at 25° C (except for SW*).

	Milimoles in Assemblage	Mass (grams)	pH (initial)	pH (Final)
Brine	Calcite			
SW	-0.0193	0.002	7.80	7.96
SWCCOA	-0.8652	0.087	5.94	7.33
LSSW10	-0.0881	0.009	7.20	9.19
LSSWCCOA	-10.160	1.016	3.70	6.09
LSSWCCOE	-0.1231	0.012	6.36	8.95
Brine	Dolomite			
SW*	0.01390	0.001	7.80	7.44
SWCCOA	-0.3550	0.035	5.94	6.95
LSSW10	-0.0211	0.002	7.20	8.86
LSSWCCOA	-5.3720	0.537	3.70	6.13
LSSWCCOE	-0.0431	0.004	6.36	8.58

A brief analysis of the effect of pH was performed to determine if crude oil/injected water interactions are relevant using the Figure 2. The progression between the initial pH of the brines in equilibrium and the final pH of the aqueous phase after the equilibrium with the rock and the crude oil for each system is shown in Table 6. From the Table, it is evident that the pH is progressing when is in contact with the rock but once the crude oil arrives, the pH declines.

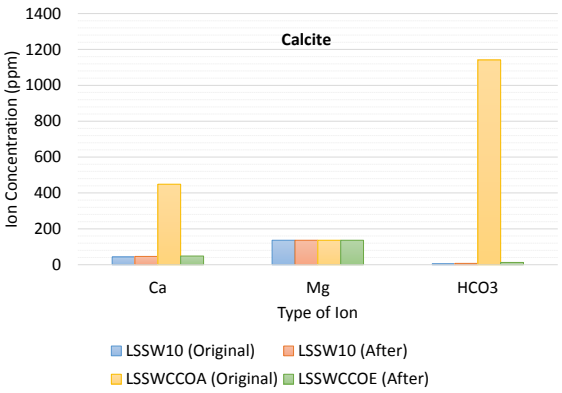

Figure 7. Calculated concentrations for calcium, magnesium and carbonate after interaction with calcite.

For systems (Oil/FW/Rock) and (Oil/FW/Rock/IW), the change is sometimes small but a perceptible decrease in the pH of system (Oil/Rock/IW) is particularly observed for the dolomite rocks. A most significant decrease in the pH for this rock indicates a surface which is less active. By definition, dolomite is chemically less active than its limestone counterpart.

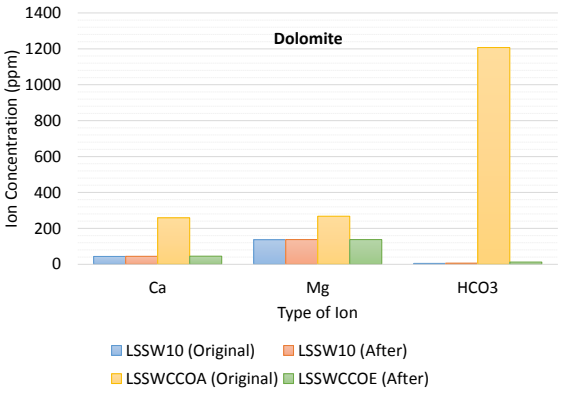

Figure 8. Calculated concentrations for calcium, magnesium and carbonate after interaction with dolomite.

The pH of the systems with the crude oils (Oil/Rock/IW) is around 7.45 and 7.30 for limestone and between 6.5 and 6.9 for dolomite. This drop is perhaps explained by the fact that the crude oil compounds interact with the aqueous solution in a different way. The dissolution of the rock is more aggressive for limestone, implying more dissolution, as previously described above.

Table 6. Behaviour of the pH for each tested system.

	Oil/FW /Rock	Oil/FW/ Rock/IW	Oil/Rock /IW
Systems with Crude Oil "A"	Limestone		
Brine	8.01	7.75	7.20
Brine (s)/Rock	8.39	7.99	8.16
Brine (s)/Rock/Crude Oil	7.93	7.87	7.46
Brine(s)/Crude Oil*	8.02	8.01	3.70
	Dolomite		
Brine	8.01	7.75	7.20
Brine (s)/Rock	8.50	8.05	7.50
Brine (s)/Rock/Crude Oil	8.10	7.97	6.55
Brine(s)/Crude Oil*	8.02	8.01	3.70
System with Crude Oil "E"	Limestone		
Brine	8.01	7.75	7.20
Brine (s)/Rock	8.39	7.99	8.16
Brine (s)/Rock/Crude Oil	7.76	7.74	7.34
Brine(s)/Crude Oil*	7.98	7.85	6.36
	Dolomite		
Brine	8.01	7.75	7.20
Brine (s)/Rock	8.50	8.05	7.96
Brine (s)/Rock/Crude Oil	7.74	7.72	6.85
Brine(s)/Crude Oil*	7.98	7.85	6.36

*Previously analysed.

Therefore, the limestone surface releases more material, which leads to higher pH values in comparison to the dolomite surfaces, where the capacity for dissolution is limited (Table 5). The low pH value of the brine (3.7) for crude oil "A" is linked to the presence of an acidic water, indicating that there is a stronger influence of the water-soluble compounds from crude oil "A" in these systems.

The impact of the crude oil in all the systems is shown in Figure 9. The pH values for the phases in equilibrium and the systems affected by an invading phase (Mix of brines/Crude Oil/Rock) stay constant. In contrast, from the second system (Mix of brines/Crude Oil/Rock) to the final system where the rock, injected fluid (LSSW10) and crude oil are all present, the changes in the pH are substantially governed by the reactions between both fluids. The initial and intermediate systems are dominated by the existence of formation water. This is not surprising, because the high salinity maintains stable conditions. As soon as the system is dominated by the low salinity water (less amounts of high salinity water), the dependence on the fluids' interaction is greater. It can also be seen from Table 6 that the initial and intermediate phases are similar when the pH of the fluid/fluid interaction is above 6. However, when the pH of the aqueous phase is ≤ 6, the final system

tends to be modified or altered. Undoubtedly, there is a reorganization of the crude oil compounds, allowing some of them to migrate to the water of low salinity by creating more acidic conditions in the system thus encouraging the dissolution of the rock.

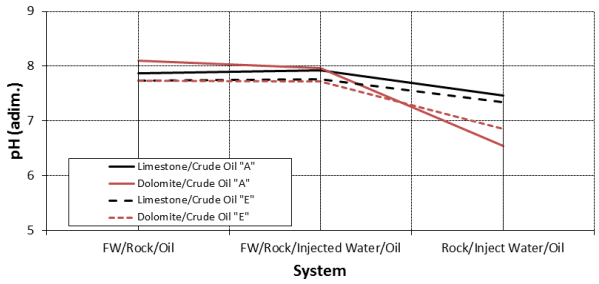

Figure 9. pH vs different systems for two carbonate formations.

To monitor a possible interchange of ions during this group of tests, samples of the brines were collected and analysed before and after the contacts. The brine composition analyses did not reveal any major changes or modifications in ion concentration of the brines. For instance, the concentrations of Ca^{2+}, Mg^{2+} and SO_4^{2-} showed a very small variation. The temperature and gently shaking the glasses were not contributing elements for large alterations in the findings.

Coreflood Experiments. Since it has been analytically established that the interactions of crude oil/smart water (especially low salinity waters) can naturally generate acidic water during water injection in carbonate rocks, the goal of this subsection will be the validation of these observations. The lack of equilibrium in the fluid/rock system may be the underlying cause of changes in wettability and rock dissolution due to such chemical interactions between invading fluids and the initial native fluids, principally with the crude oils. For this reason, one cannot confirm these facts without considering the flow of fluids throughout the cores at reservoir conditions. Moreover, the possibility that these conditions would involve the pressure and its influence cannot be excluded either. Considering that dissolution has been identified as part of the effects that occur during smart water injection, especially in low salinity waters, coreflood experiments should enable us to observe the difference in the enhanced oil recovery if different brines and crude oils are used. This will make it possible to distinguish where and when this vital mechanism occurs.

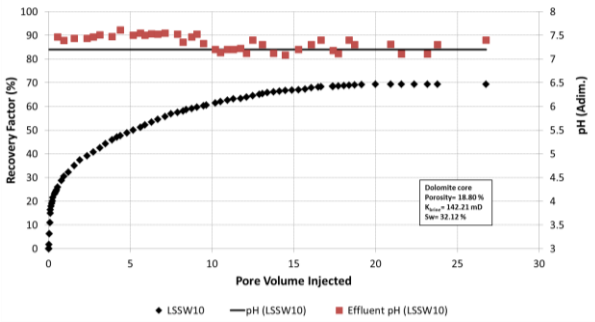

Figure 10. Cumulative oil recovery for a dolomite core with LSSW10 at 92° C.

As indicated previously in this work, there is probably a pattern that proves that dissolution plays an important role during the additional oil production. Therefore, we will mainly focus on more elaborate experiments such as coreflood experiments where it will be demonstrated how the simple models previously presented can be used to predict if dissolution of the rock is taking place in the fluid/rock interaction and then to evaluate its impact on final oil production. Coreflood experiments were then carried out under secondary injection mode, in order to experimentally investigate the performance of smart water injection for heavy oils. Water composition changes, pH measurements, permeability variations and oil recoveries before and after the experiments were all performed during the experiments. That will allow us to examine the fundamentals of fluid flow and analyse whether changes occur, where they occur and how they are influenced by the injected waters. The results will supplement previous findings.

For the coreflood experiments the crude oil "A" was selected and a dolomite core was firstly flooded with a diluted version of seawater (10 times) as a secondary process. Pressure, pH and effluent composition were constantly monitored (Figure 10). After 22 pore volumes were injected, a 24-hour soak period was applied. No extra oil was recovered after this closure. Because of the high permeability of the core, a high rate was applied at the end of each stage (20 cm^3/hr). The LSSW10 injection resulted in the final recovery of 69.30 % OOIP. With respect to pH, after rising slightly and staying stable during injection of 9.5 pore volume, it fell at 10 pore volumes injected and fluctuated between 7.2 to 7.3 units.

For the effluents of the LSSW10 injection period (Figure 11), it may be clearly seen that the calcium and bicarbonate concentrations rose and those of sulphate and magnesium also exhibited small variations. The effluent samples were treated with methyl orange and then titrated with hydrochloric acid once it was not possible to detect bicarbonate concentrations using ion chromatography analysis. The concentrations of the rest of the elements remained constant (sodium, potassium and chloride). This production may be linked to the reaction of the injected water, firstly with the crude oil and subsequently with the rock, leading

to a possible dissolution effect. Later, this assumption was supported by the measurement of the new permeability, which turned out to be higher, 180.28 md. Permeability changes were studied using Darcy´s Law. A tertiary programme was not applied for this test.

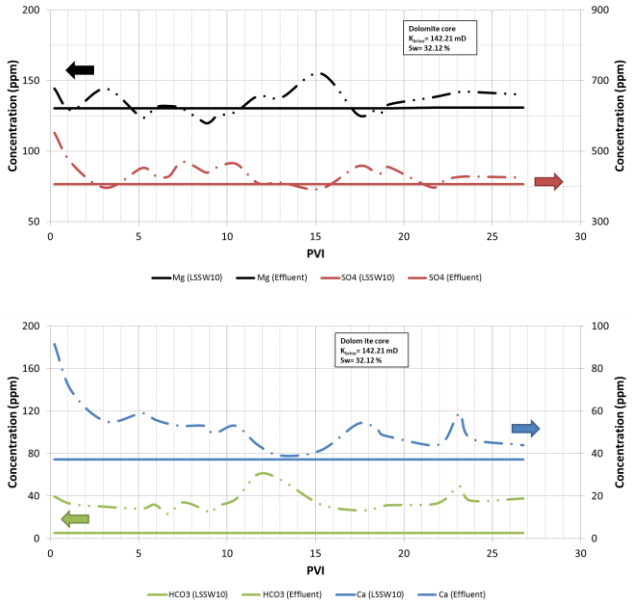

Figure 11. Changes in ion concentration of calcium, magnesium, sulphate and bicarbonates when low salinity water is flooded through a dolomite core at 92° C.

Once the experiment with low salinity seawater was finished, the core was cleaned and reused later. The same process was repeated, except the type of injected brine was changed. This time, the core was brought into contact with seawater. High oil volume was produced at early time. Before 4 pore volumes had been injected, the recovery factor was around 31 %, as shown in Figure 12. From 5 to 10 pore volumes, the recovered oil was around of 2 % more. Later, pH measurements were obtained from the effluents. The pH tended to drop from 7.8 to 7.0, approximately. Alotaibi et al.[35] obtained similar results using dolomite cores at 90° C. In their tests, the recovery factor was around 35.5 % after 2.5 pore volumes.

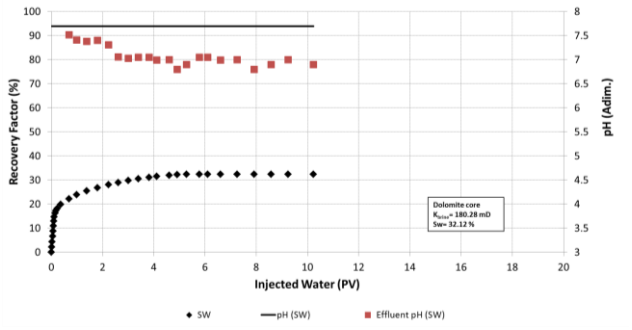

Figure 12. Oil recovery versus pore volumes of injected seawater at 92° C.

The reactivity of the core towards the divalent ions appeared to be negligible, except for magnesium, Figure 13. This divalent ion and also sulphur showed small variations on their concentrations, staying active at high temperature. The bicarbonate ion was completely inert.

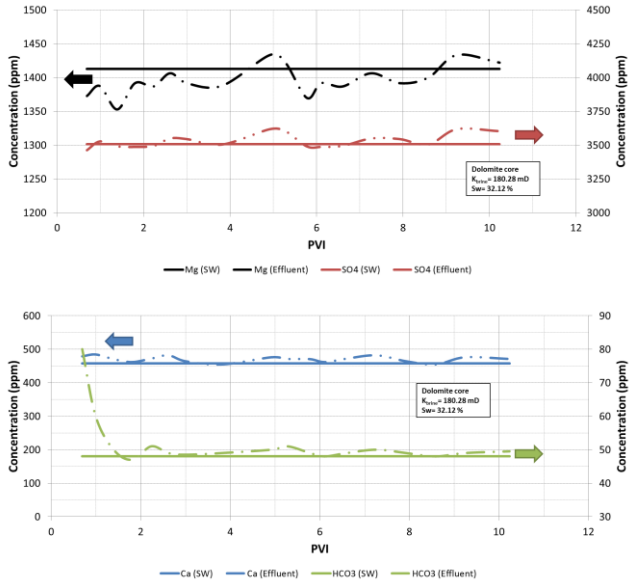

Figure 13. Changes in ion concentration of calcium, magnesium, sulphate and bicarbonates when seawater is flooded through a dolomite core at 92° C.

Calcium, magnesium and sulphate have been reported as potential determining ions for improving oil recovery in carbonate rocks. For these experiments, the effect of such ions on the wettability change is not in good agreement with the results described by Austad's group[4,6,36,37, 38,39]. However, there is a contrast between the ion evaluation and the permeability measurements after the experiment. The water permeability decreased dramatically to a stable value of 64.08 md, which was around 65 % below its initial permeability (180.28 md). The decrease in permeability denotes that the permeability was dominated by the damage resulting from the seawater injection. The lack of ion production and the loss of permeability may be linked to this damage caused by seawater injection. Overall, this core was found to suffer permeability loss when seawater is used as a smart fluid.

From the differential pressure curves in Figure 14, it is evident that during each experiment, the pressure first increased then decreased slowly, and later the trend was stabilised. In addition, from this Figure, some small variations of pressure were noticed when both high rates and shut-in periods were applied. Thereafter, other major changes in pressure were not detected or the differential pressure response did not give an indication of any instability and hence unusual behaviour.

For dolomites, the seawater was supersaturated (SI>0, Table 4) at high temperatures. That is, the seawater is fully saturated with diverse ions in solution, so, this state does

not allow that material from the rock become dissolved and/or transported. Thus, this condition of saturation set up the potential for particular events such as precipitation, pore blocking (plugging) or loss of permeability. In the case with inject seawater, it is clear that saturation condition of this fluid will favour the permeability reduction (up to 65 % for the dolomite core), as shown in Table 7. If the saturation index is negative (SI<0), as for the low salinity waters shown in Table 4, then no precipitation will take place. Consequently, the low salinity waters may adequately dissolve and transport the released material from the rock, which originated from the action of the acidic water derived from the crude oil/low salinity brine interaction. Over the long term this process will lead to improving the internal conductivity in the porous media, generating a better permeability, as seen in Table 7 for low salinity water injection (from 142.21 to 180.28 md, respectively).

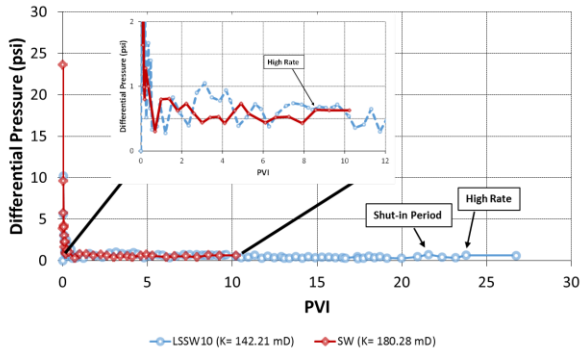

Figure 14. Differential pressure cross core versus pore volumes for the dolomite core with two brines.

Dissolution of the rock is usually studied in the context of room conditions and hence research for elevated temperatures or pressures is limited in the published literature[40,41,42]. For instance, calcite and dolomite minerals have been investigated in terms of the importance of transport control vs pH changes. When the temperature goes up diffusion will control the system. At low temperatures, dissolution is a chemical control mechanism[43,44,45,46,47,48,49].

Table 7. Changes of core permeability after coreflood experiments.

Initial K_{brine} (mD)	Process	Injected Fluid	RF (%)	Final K_{brine} (mD)
142.21	Secondary	LSSW10	69.30	180.28
180.28	Secondary	Seawater	32.43	64.08

Morse and Arvidson[50] compiled dolomite dissolution data as a function of pH from published values. The experiments of Zhang et al.[40] indicate that the mechanisms of dissolution of dolomite at low temperatures differ from those at high temperatures. Their results indicate that there are linear correlations between concentrations of calcium and magnesium in the aqueous phases. The release rates of calcium and magnesium are proportional (1:1), especially at temperatures below 100 °C. However, the dissolution product is incongruent at higher temperatures. The concentration of dissolved calcium did not show a linear correlation with magnesium concentration in the effluents. Their observations were in line with Morey's work in the early 60's[42]. Both observations were congruent up to as high as 80° C (1:1 dissolution) but above that the solution was non-stoichiometric (unequal proportions for a specific chemical reaction).

In addition, a rise in the dissolved concentration of calcium or magnesium in the aqueous solutions usually decreases the dissolution rate for the calcite. In this case, the named ions may act as inhibitors. The function of the inhibitors for calcite was exhaustively reviewed in Morse and Arvidson's work[50]. On the other hand, Zhang and al.[40] found that dissolved calcium is a strong inhibitor for dolomite dissolution, in most cases. Magnesium was found to be less active as an inhibitor at low temperatures but at high temperatures (from 100 to 250° C), dissolution rates of dolomite were increased with increasing in the concentration of dissolved magnesium.

Thus, a vast number of studies have provided evidence that the rate of dissolution is highly dependent on diverse variables. Under reservoir conditions where such variables are important, smart waters may then apparently mobilise the released material from the core and produce/transport it to the outside. The observation that smart waters may mobilise this material also suggests that movement and transport are likely to occur during coreflood experiments, in either secondary or tertiary oil recovery methods at high pressure and high temperature, even at reservoir scale, where reservoir conditions could favour better situations for dissolution and transport. Therefore, dissolution studies have help to better understand and verify many of the variables which are taking part during the dissolution in coreflood experiments such as pressure, temperature, rate controlling mechanisms, type of aqueous phase, pH and ionic strength, and CO_2 content or the presence of inhibitors.

CONCLUSIONS

The effect of the aqueous phase pH and the ion interactions between fluids and rocks was investigated at static conditions. The results highlighted that the initial, intermediate and final systems all depend on the interaction of the fluids. The behaviour of the fluids in interacting would be more representative under dynamic conditions. With the flow of fluids, dissolution should be increased. The main results obtained in this research have indicated that the nature of the acidic species in the crude oil enables them to become important agents and firstly cause a reaction between the crude oil and the brine of low salinity. The solubility of certain oil compounds increases in the aqueous phase, due to the low salinity concentration. The

findings from these experiments then revealed the generation of acidic water, which is derived from the interaction between injected fluids and crude oils. The effect on oil recovery from the low salinity water may then be partly due to the chemical reaction between the diluted water and the acids that exist in the crude oil.

The water-soluble compounds dictate whether acidic water is generated or not. For the basic crude oils tested in this work, all of them generated acidic water, which is the cause of rock dissolution, from low salinity water to distilled water. On the other hand, acidic crude oil was the only one that did not generate acidic water, but this does not mean that there is a rule for all the crude oils. The key parameter is the amount of water-soluble compounds that the crude oils contain.

These results question the link between a high amount of acidic components and generation of acidic water and unequivocally indicate that it is not conclusive or sufficient. Therefore, it is necessary to investigate in more detail the content of water-soluble compounds in the acidic crude oils. In this work, practical analysis helped to elucidate the real importance of the crude oil/injection water interactions. The tests that were presented in this research essentially provide an insight into the impact of the chemical interaction between crude oil and injection water with the rock. Based on direct evidence, basic assessments aided in understanding why:

a) The solubility of certain oil compounds (water-soluble compounds) increases in the aqueous phase,

b) The acidic water is generated,

c) The crude oil can be detached from the rock surface when the equilibrium in the system is broken,

d) Rock dissolution takes place,

e) The pH of the effluents is increasing in value.

The influence of crude oil properties has largely been overlooked in the literature because it was assumed that both crude oil and injection brine were immiscible or remained unaffected in contact with each other. The findings from recent works have challenged this assumption and the research in this work corroborates these findings and confirms that crude oil/injection water interactions do really occur.

This research has allowed that even in basic analysis, the interaction between the crude oil and the injected water is meaningful. In reality, the chemical interaction between crude oil and injected water may be one of the main reasons for the increased efficiency in response to the use of the smart waters for the improvement of oil production.

The suggested model in Figure 6, as previously stated, supports the assumption that basic crude oils can be susceptible to donating hydrogen ions in the case analysed, generating acidic water. This proposed model cannot be generalised to all basic crude oils or ruled out for all acidic crude oils. The components of crude oil, as observed, will dictate what type of interactions will occur between the injected water and the crude oil.

The effect of this generated water on rock dissolution has been studied in more details at dynamic conditions in a dolomitic core. The tests of these studies proved that is possible to predict the occurrence of the dissolution phenomenon during smart water injection using simple fluid-fluid contact tests.

Effluent analysis and permeability evaluations validated the influence caused by low salinity water as acidic water in contact with the rock. The presence of rock dissolution was principally detected by coreflood experiments through changes in ion concentrations of calcium and bicarbonates. There is no doubt that the effect would be more important at reservoir scale once that is the crude oil, itself, an important agent playing a vital role for the improvement of oil production. These findings differ from Mahani et al.[51,52] where they affirmed that the rock dissolution was only relevant on a laboratory scale and not at reservoir scale. Inevitably, we all sometimes see things subjectively, to some extent, or with the lack of strong evidence.

Damage to the core occurred when seawater was used for improvement of the oil production. Permeability measurements corroborated these findings. Positive effects derivate from the use of seawater were not observed here.

In spite the fact that the permeability changes occurred, no direct experimental evidence is accessible to support the possibility that either dissolution or blockage can be detected by analysing differential pressure across the used core, so far.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

Authors acknowledgement the financial support for this work provided by the National Council of Science and Technology and the Ministry of Energy of Mexico (Conacyt-Sener-Hicrocarburos). The authors also wish to thank Tom Scott for designing some figures for this research.

NOMENCLATURE

CND	Carbon Number Distribution
DW	Distilled Water
FW	Formation Water
IAP	Ion Activity Constant
IFT	Interfacial Tension
K	Equilibrium Constant
LSSWCCOA	Low Salinity Seawater after the Contact with Crude Oil "A"
LSSWCCOE	Low Salinity Seawater after the Contact with Crude Oil "E"
LSSW10	Low Salinity Seawater, 10 Times
LSSW50	Low Salinity Seawater, 50 Times

pKa	Acid Dissolution Constant
pKb	Base Dissolution Constant
SI	Saturation Index
SW	Synthetic Water
TAN	Total Acid Number (mgKOH/g)
TBN	Total Basic Number (mgKOH/g)

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